(51) International Patent Classification 7 : C02F 1/68, 1/26	A1	(11) International Publication Number: WO 00/58225
		(43) International Publication Date: 5 October 2000 (05.10.00)

(21) International Application Number: PCT/GB00/01251

(22) International Filing Date: 31 March 2000 (31.03.00)

(30) Priority Data:
9907485.8   31 March 1999 (31.03.99)   GB

31 Sep 01 30 Mun

(71) Applicant (*for all designated States except US*): THE UNIVER-SITY COURT OF THE UNIVERSITY OF EDINBURGH [GB/GB]; Old College, South Bridge, Edinburgh EH8 9YL (GB).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): TASKER, Peter, Anthony [GB/GB]; 25 Braid Avenue, Edinburgh (GB). WHITE, David, James [GB/GB]; 3 Roachill Close, Altrincham, Cheshire (GB).

(74) Agent: MANATON, Ross, Timothy; J.Y. & G.W. Johnson, Kingsbourne House, 229–231 High Holborn, London WC1V 7DP (GB).

(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS

(57) Abstract

A method of removing both the cations and the anions of a metal salt from an aqueous medium, by use of a ligand having binding sites for the cations and anions. The cation binding site comprises at least one coordinating acid group and the anion binding site comprises at least one protonatable base. Using ligands of this type, both the anions and cations may be selectively stripped from the ligand and recovered, and the ligand may thereby be recycled for further use.

EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS

Field of the invention

5   This invention relates to the extraction of metal salts from aqueous solutions. More specifically it relates to methods for extracting metal cations and their associated anions which avoid returning any ionic species to the solution, thus leaving the acidity of the solution unchanged and purifying it by de-ionisation. Methods according to the invention are of use particularly (though not

10   exclusively) in waste remediation and in the recovery of metals from primary sources.

Background

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Two main methods are currently used for the extraction of metallic ions from solution. Both involve the use of an extractant reagent: in the first method this is mixed with the solution from which the metal ions are to be removed ("solvent extraction"), and in the second it is immobilised on a solid support.

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Current solvent extraction technology is based on the reaction scheme shown schematically in Figure 1. In this system an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on

25   the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

This type of reaction is widely used for the extraction of copper from oxidic ores, the acid introduced into the stream reacting with insoluble metal oxides to

30   give soluble metal salts. Indeed, this reaction scheme is particularly suited to the extraction of metals from metal oxides since the overall reaction has a perfect mass balance equation:

$$MO + Power = M + \tfrac{1}{2}O_2$$

However, this extraction technique suffers from a number of shortcomings. For instance, it is not suitable for use in relation to feed streams which have a very high metal tenor (i.e. a high concentration of metal in the feed), since removal of metal ions rapidly decreases the pH of the solution, and this renders the extractant ineffective. A similar effect is observed if the feed stream itself has a low pH value. For the same reason, if acid is not consumed in the leach process, pH will decrease and the extractant will become ineffective unless action is taken to neutralise the stream. This is particularly important in oxidative pressure leaching of sulfidic metal ores and biological leaching of sulfidic ores, where oxygen or oxygen and microbes are used to convert sulfides into sulfates without consumption of acid. Furthermore, the waste water from such extraction techniques cannot be discharged to the environment after metal extraction since, again, neutralisation of the acid would be required prior to discharge.

As far as solid supported reagents are concerned, most of these operate as ion exchange materials. The reagent on the solid phase support binds a metal cation and releases a cation (usually Na^+ or a proton) to the aqueous phase. Thus, the metal ion in solution is replaced either by sodium ions which increases the salinity of the solution, or by protons which reduce the pH of the feed solution. In either case the anion is left in solution.

We have now found that it is possible, through careful engineering of the ligand, to extract metal cations from a solution and simultaneously to extract their associated anions. This method has the advantage that the whole metal salt is removed from the feed stream, the pH of the stream is unaltered, and no additional species are added to the feed stream. Additionally, the ligands we have developed permit both the anions and the cations to be recovered by stripping methods, with the result that the ligand may then be reused.

The ligands of use in the method of the invention have binding sites for both cations and anions, in contrast to the vast majority of existing ligands which

bind only cations. A small number of bifunctional ligands have been identified in the past, and some of these are reviewed in "Comprehensive Supramolecular Chemistry" (1996) Chapter 18 "Simultaneous Binding of Cations and Anions" (Manfred T. Reetz) pp 553-562. A common feature of the ligands described is

5   that the cation binding sites are all ordinary or azo crown ethers. A variety of groups are suggested for anion binding, such as polyammonium, guanidine, boronic acid and cobalticinium. Crown ethers are also suggested as the cation binding site of bifunctional ligands by Ezzidin et al (J. Chem. Soc [1992] 61-64), Olsher et al (J. Am. Chem. Soc. 113 [1991] 6570-6574) and Flack et al (J. Chem.

10   Soc., Chem. Commun. [1993] 399-401). Nitrogen-containing groups provide the anion binding sites of the ligands proposed by Ezzidin et al and Flack et al, while Olsher et al use alcohol groups.

Alternative ligands are proposed by Hogerhide et al (Inorg. Chem. 35

15   [1996] 1185-1194), Pelizzi et al (J. Chem. Soc., Perkin Trans. 2 [1998] 1307-1311) and Savage et al (J. Am. Chem. Soc. 116 [1994] 4069-4070), but as with the papers relating to crown ether ligands referred to above, there is no suggestion of recovery of both anions and cations in any ready manner. The target metal salts are almost exclusively those containing small monovalent

20   metal cations such as Na^+ and K^+. Transition metal salts are not considered.

Shanmuga et al (Acta Crystallographica Section C [1999] 94-97) mention a ligand identical with that identified in the description below as ligand 4. However, the authors propose this for use solely in forming binuclear metal

25   complexes as models of metal binding in biology. There is no suggestion or intention to bind either anions or metal salts. Additionally, no real evidence of metal binding is provided.

30   <u>Summary of the invention</u>

The invention seeks to overcome the drawbacks associated with the existing methods for metal salt removal, and provides a method of extracting

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both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the steps of: contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s); selectively stripping and recovering said cation(s) and said anion(s) from said complex; and recovering said ligand, free of said cation(s) and anion(s), for future use. The method is particularly suitable for use with transition metal salts (including salts of the lanthanides and actinides)

The method of the invention may either be carried out as a solvent extraction process of by use of a solid phase ligand. In the solvent extraction process, the ligand preferably has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, which may readily be achieved by judicious choice of side chains to render the ligand substantially hydrophobic. Preferably, the method involves the steps of adding the water-immiscible extraction medium to the aqueous medium (whereby the ligand with the cation(s) and anion(s) bound thereto is partitioned preferentially a water-immiscible phase), and separating the water-immiscible phase with the cation(s) and anion(s) therein from the aqueous phase.

For operation as a solid-phase extractant, the ligand may simply be immobilised on a solid support. By contacting the support-bound ligand with the aqueous feed stream, the metal salt may thereby be removed in a simple one-step process, without the need for a separation step. A solid-phase extraction is particularly useful for sequestering species from dilute solutions, in respect of which solvent extraction tends to be cumbersome and inefficient. The method will be particularly useful in the remediation of contaminated streams, especially those which are acidic, for example in the removal of actinide salts produced in the nuclear industry.

In both solvent and solid based methods, metal cations and their associated anions removed from the solution simultaneously, and no species are returned to the feed stream in their place. This makes the processes suitable for

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use in many applications for which the prior art methods are unsuitable, since the pH of the feed stream is unaltered, the feed stream is purified by de-ionisation, and, within limits that will be defined by the specific reagent used in the process, metal cations and anions can be extracted at low pH without further lowering the pH. For the sake of simplicity and clarity the invention will hereafter be described principally with respect to solvent extraction processes, but the skilled man will have no difficulty in adapting the techniques for use in analogues solid-phase systems.

The applicants have developed two distinct classes of ligand for use in the processes of the invention. The first class ("Type I") have the following general formula:
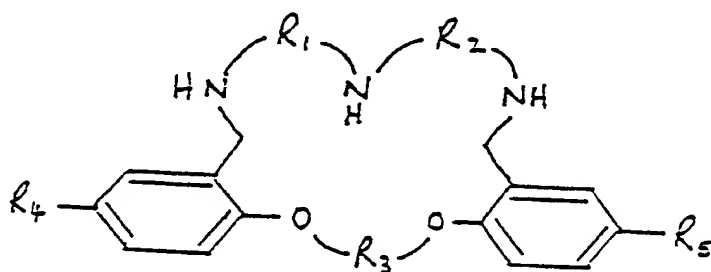
where: R_1, R_2 and R_3 are, independently, optionally substituted C_2 to C_4 linkages;

           R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

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The second class ("Type II") have the formula:
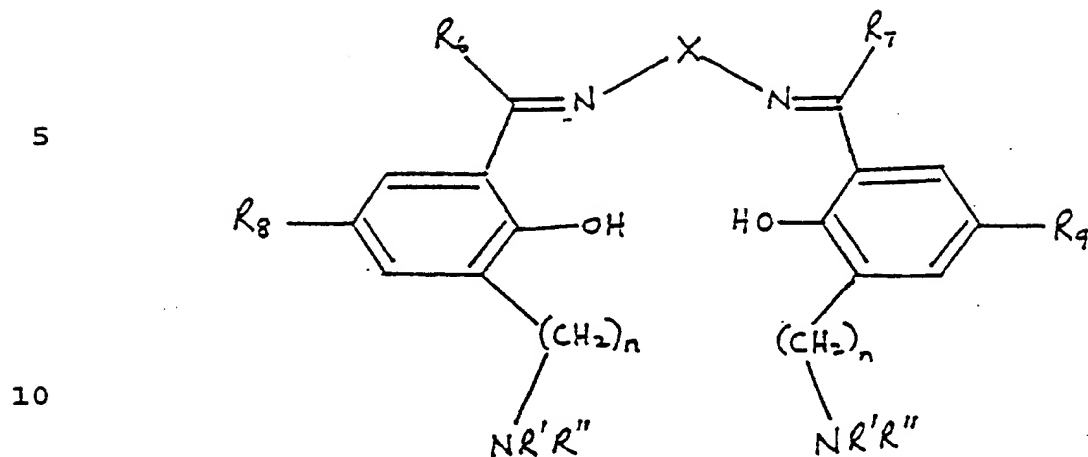
where: X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

NR'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

In both cases the side chains (R_4, R_5, R_6, R_7, R_8 and R_9) do not take part in ligand binding, and may be freely chosen with reference to the nature of the extraction medium in order to afford maximum solubility of the ligand therein. Hydrocarbon extraction media are preferred, and thus the side chains will normally confer hydrophobicity.

In the Type II ligands, it is believed that the metal cation binds first to the nitrogen atoms of the C=N groups and to the phenolic oxygen atoms. The

phenolic protons are then displaced and protonate the nitrogen atoms of the tertiary amine groups, producing a positively charged binding site for the anion. The precise binding mechanism for the Type I ligands has yet to be elucidated.

5   Use of either class of ligand is effective to remove both the cations and anions of a metal salt from the feed stream. When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases however, it is desired to extract the cations as elemental metal, and indeed this is the primary aim of ore extraction methods. A major

10   advantage of the method of the invention is that the anion may also retrieved; for instance the anion (such as sulphate) may be precipitated as an ammonium salt, which may then be used as fertiliser. As a result, this ligand is regenerated in unbound form, and may be recycled for future use.

15   The method of cation and anion precipitation depends on the class of ligand. For Type I ligands, contact with an aqueous ammoniacal solution liberates an ammoniacal solution of the metal salt from which the metal can be electrolysed. The electrolysis step produces metal and acid. Continual addition of ammonia to the system is required to neutralise the acid produced, and a by

20   product of the reaction is an ammonium salt. For Type II ligands, the metal cation may also be recovered by contacting with strong acid. The metal cation M^{n+} in the hydrocarbon solution is replaced by n protons generating the 'acid' form of the reagent LH_nX. This allows electrolysis of the metal from an acidic medium. The resulting solution is then contacted with ammonia solution,

25   regenerating the reagent L and producing an ammonium salt as a by product.

In each case the overall reaction is the same, and may be represented by the reaction scheme illustrated in Figure 2. The overall mass balance for this system is:

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$$MS + 1\tfrac{1}{2}O_2 + H_2O + 2NH_3 + Power = M + (NH_4)_2SO_4$$
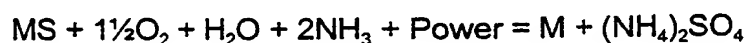
In a waste remediation application, for example removal of metal salts

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from acid mine drainage streams, the reaction scheme is illustrated in Figure 3; the overall mass balance is:

$$MSO_4 + H_2O + 2NH_3 + Power = M + (NH_4)_2SO_4 + \tfrac{1}{2}O_2$$

5

The Type I ligands are known in the literature, though not for the purpose of removing metal salts from aqueous solutions as in the present invention; their synthesis will therefore not be described herein. To illustrate the efficacy of ligands of this type in removing metal salts from aqueous solution, a 0.1M

10   solution in toluene of Type I ligand ($R_1 = R_2 = R_3 = -CH_2CH_2-$; $R_4=R_5= C_9H_{19}$) was contacted with a 0.1M aqueous solution of nickel sulfate. A light blue toluene solution was formed, analysis of which showed that approximately 80% of both Ni^{2+} and SO_4^{2-} ions had been transferred to the organic phase.

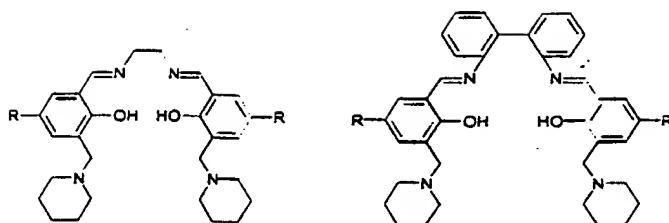15   <u>Detailed description</u>

The invention is described hereinafter in more detail with reference to the synthesis and activity of various ligands of the Type II formula. The following is a representative sample of various different Type II ligands:

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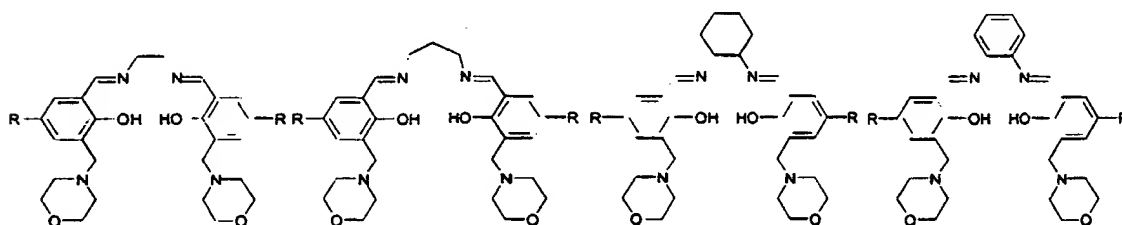
25

Me	4	5	6	7
TBu	8	9	10	11
Nonyl	12	13	14	15

9

Me	16	17
Tbu	18	19
Nonyl	20	21

By way of example, X-ray structure studies have demonstrated that the mode of binding of nickel nitrate and nickel sulfate to ligand number 8 is generally as shown below. As will be seen, the protons liberated from the phenolic groups in the metal binding site remain incorporated in the ligand, and protonate the basic pendant morpholine groups to form the anion binding site(s).
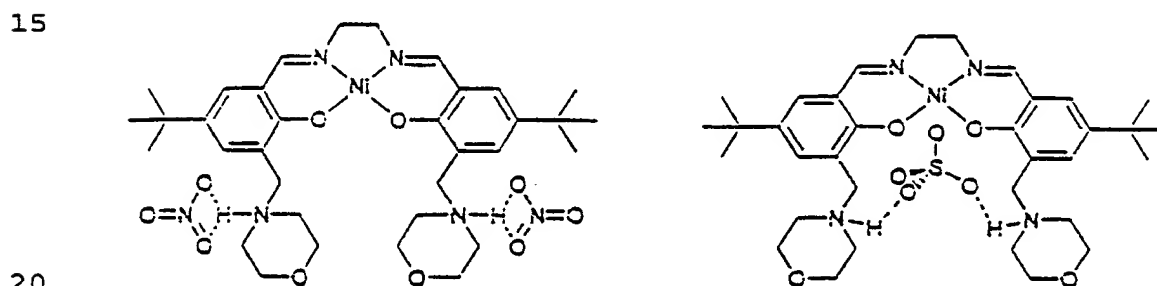
Solvent extraction studies have been carried out to characterise the extraction behaviour of these ligands, and are summarised in the experimental sec tion below. In order for the extraction system to be viable a plateau pH range must exist at which both metal cation and sulphur are extracted with 100% efficiency. This can be engineered into the molecule by judicious choice of chelating moiety and internal base.

Synthesis and characterisation of ligands

The invention will now be exemplified by reference to the following experimental results relating to the synthesis of various ligands, their use in chelating various metal salts, and the subsequent stripping of both anions and cations from the ligands.
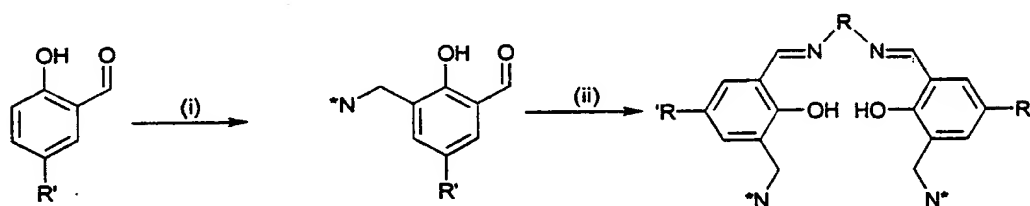
The ligands may be produced according to the following general reaction scheme, which is based on Schiff base type SALEN chemistry:

Where N* = a tertiary amine, for example a ring structure such as morpholine or piperidine.

The starting 2-hydroxy-5-alkyl benzaldehydes were prepared by the method of Levin (R. Aldred, R. Johnston, D. Levin, and J. Neilan, J. Chem. Soc. Perkin. Trans. 1, 1994, 1823) and the 4-ethoxymethyl morpholine/4-ethoxymethyl piperidines and hydroxy-3-(morpholin-4-yl-methyl)-benzaldehydes by the methods described by Fenton. (H. Adams, N. A. Bailey, D. E. Fenton, and G. Papageorgiou, J. Chem. Soc. Dalton. Trans., 1995, 1883).

Examples of these ligands were produced as follows:

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Synthesis — N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine (ligand 8).

2-Hydroxy-3-(morpholin-4-yl-methyl)-5-tert-butyl-benzaldehyde (6g, 21.7 mmol) was dissolved in diethyl ether (60ml) and added to a solution of ethane-1,2-diamine (0.636g, 10.6mmol) in ethanol (60ml). The resulting yellow solution was stirred overnight then concentrated in vacuo to give a yellow oil which on trituration in hexane at –78°C gave a waxy yellow solid. This was washed with hexane (15ml) and ether (15ml) and dried in vacuo (5.8 g, 95 %). m.p. 155-158 °C. (Found: C, 70.60; H, 9.06; N, 9.67. Calc. for $C_{34}H_{50}N_4O_4$: C, 70.56; H, 8.71; N, 9.68%). δ_H (CDCl$_3$, 200 MHz): 1.28 (s, 9H, C(CH$_3$)$_3$), 2.50 (t, $^3J_{HH}$ 4.6 Hz, 4H, NCH$_2$CH$_2$O), 3.58 (s, 2H, NCH$_2$CH$_2$N), 3.71 (t, $^3J_{HH}$ 4.6 Hz, 4H, NCH$_2$CH$_2$O), 3.90 (s, 2H, Ar-CH$_2$N), 7.14 (d, 1H, $^4J_{HH}$ 2.5 Hz, Ar-H), 7.37 (d, 1H, $^4J_{HH}$ 2.5 Hz, Ar-H), 8.37 (s, 1H, N=CH), 13.23 (s, br, 1H, OH). δ_C (CDCl$_3$): 31 (CH$_3$), 34 (C(CH$_3$)$_3$), 53 (NCH$_2$CH$_2$O), 57 (CCH$_2$N), 60 (NCH$_2$CH$_2$N), 67 (NCH$_2$CH$_2$O), 118 (Ar C), 124 (Ar C), 127 (Ar CH), 131 (Ar CH), 141 (Ar C), 157 (Ar C), 167 (CHN). MS (FAB, thioglycerol) m/z 579 (MH$^+$, 62 %).

Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] 1,3 – Diamino Propane (ligand 9).

5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (6.000g, 21.7 mmol) was dissolved in diethyl ether (60ml) and poured into a solution of 1,3 – diamino propane (0.786g, 10.6mmol) in ethanol (60ml). Colour changed instantly to yellow and the solution was stirred overnight. Removing the solvent in vacuo gave the product as a dark yellow oil which was triturated in hexane at –78°C to produce a waxy yellow solid. Washed as above. MP 126-128 °C. Calculated for $C_{35}H_{52}N_4O_4$ – 70.91%C, 8.84%H, 9.45%N, found 70.15%C, 9.05%H, 9.37%N. FAB-MS m/z, normalised intensity, [assignment]: 594, 621.8% [MH$^+$]; 505, 18.9%, [M$^+$ - morph – 2H]; 422, base peak, [MH$^+$ - 2morph]. NMR (CDCl$_3$) ^{1}H: δ 1.30 (s, 9H, ^{t}Bu), 2.08 (t, J=6.5, 1H, centre propyl methylene), 2.52 (t, J=4.1, 4H, propyl and benzylic), 3.61, (s), and 3.66 (m, J=4.6, 8H, morpholinyl), 7.16 (d, J=2.5, 1H, aryl), 7.40 (d, J=2.5, 1H, aryl), 8.38 (s, 1H, imine), 13.51 (s,

broad, 1H, phenolic). ^{13}C δ: 30.80 (CH_3, ^tBu), 31.32 (CH_2, centre propyl methylene), 33.80 (q, ^tBu), 53.49 (CH_2, morpholinyl), 56.57, 56.65 (CH_2, benzylic/propyl), 66.90, (CH_2, morpholinyl), 117.68, 124.04 (q, aryl), 126.55, 130.88 (CH, aryl), 140.52, 157.32 (q, aryl) 165.53 (CH, aldehydic). FT-IR:

5   (Dichloromethane film) 704cm^{-1} very strong, 737vs, 804w, 863s, 884m, 909m, 1007 and 1015 m doublet, 1032w, 1070m, 1116vs (dialkyl ether a.s. stretch), 1206m, 1265vs, 1303w, 1331w, 1363w, 1457w, 1457s, 1483s, 1633s, 2860vs and 2963vs (CH stretch), 3052m, 3940vw, 4195vw.

10 Characterisation of — N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] trans – 1,2 – diamino cyclohexane (ligand 10).

Ligand 10 was produced in a manner similar to ligands 8 and 9 above. This yellow solid was recrystallised from petroleum ether (40-60), collected by

15 filtration and air-dried (1.080g, 79%). m.p. 103-106 °C. Found: C, 69.19; H, 9.17; N, 8.46. Calc. for $C_{38}H_{56}N_4O_4$: C, 72.12; H, 8.92; N, 8.89%. $δ_H$ ($CDCl_3$, 200 MHz): 1.23 (s, 9H, $C(CH_3)_3$), 1.66 (m, br, 4H, cHex CH_2), 1.86 (m, br, 4H, cHex CH_2), 2.48 (t, $^3J_{HH}$ 4.5 Hz, 4H, NCH_2CH_2O), 3.30 (m, 1H, cHex NCH), 3.70 (t, $^3J_{HH}$ 4.5 Hz 4H, NCH_2CH_2O), 3.54 (s, 2H, Ar-CH_2N), 7.06 (d, 1H, $^4J_{HH}$ 2.4 Hz,

20 Ar-H), 7.33 (d, 1H, $^4J_{HH}$ 2.4 Hz, Ar-H), 8.27 (s, 1H, N=CH), 13.5 (s, br, 1H, OH). $δ_C$ ($CDCl_3$): 24.07 (cHex CH_2), 31.23 (CH_3), 31.43 (cHex CH_2) 33.70 ($C(CH_3)_3$), 53.08 (CCH_2N), 53.57 (NCH_2CH_2O), 56.65 (cHex CH_2), 59.58 (cHex CH_2), 66.84 (NCH_2CH_2O), 117.6 (Ar C), 124.0 (Ar C), 127 (Ar CH), 131 (Ar CH), 141 (Ar C), 157 (Ar C), 165 (CHN). MS (FAB, thioglycerol) m/z 633 (MH$^+$, 42%).

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Synthesis – Ethoxy–N–Morpholin-4–yl Methane.

Morpholine (87.12g, 1mole) was added dropwise to a suspension of

30 paraformaldehyde (37.64g, 1.25 mol) and potassium carbonate (276.4g, 2mol) in ethanol (500ml) at 0°C with overhead mechanical stirring. When addition of morpholine was complete, the mixture was allowed to warm to room temperature and stirred vigorously for 48 hours. After this time, the solid

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residues were filtered off and washed with ethanol (2 × 50ml), filtrate and washings were combined and concentrated under vacuum to leave a cloudy brown oil. This was distilled through a verigreux column under reduced pressure to give product as a clear, non-viscous liquid. BP 34°C at 0.3 mbar,

5   Yield = 103.12g, 0.71 mol, 71%. Calculated for $C_7H_{15}O_2N$: 57.90%C, 10.41%H, 9.65%N, Found: 55.10%C, 10.37%H, 10.35%N, EI-MS: 100m/z, base peak, $[O(CH_2CH_2)_2NCH_2^+]$, no M^+ peak observed.

Synthesis −5-nonyl-Salicylaldehyde.

Magnesium methoxide catalyst was generated in situ by refluxing magnesium

10   raspings (7.3g, 0.3 mol) and magnesium methoxide (1.75g of 7.4% w/w methanolic solution, 1.5 mmol) in methanol and toluene for 2 hours. When all the magnesium was dissolved and H_2 evolution had ceased 4-Nonyl phenol (112g, 0.5mol) was added and mixture was refluxed for a further hour. Toluene was added and the methanol −toluene azeotrope was removed by distillation at

15   85°C. A slurry of paraformaldehyde (45g, 1.5mol) in toluene was added to reaction over 50 minutes with concurrent removal of the volatile products by distillation. Stirring was continued at 95 − 100°C for 2 hours, then the mixture was cooled to room temperature. Solvent was removed under reduced pressure yielding the product as a pale yellow oil, purified by short path

20   distillation under vacuum. B.P at 120°C at 1.0 mbar. NMR ($CDCl_3$) ^1H: δ 0.46 − 1.77 (m, J=1.2 − 6.4, 19H nonyl), 6.82 (d, J=9.2, 1H, aryl), 7.45 (m J=7-9, 2H, aryl), 9.88 (s, 1H, phenolic), 10.87 (s, 1H, aldehydic). ^{13}C δ:8.36 − 52.21 (nonyl), 116.94 (CH aryl), 119.90 (q, aryl), 130.42 (CH aryl), 135.42 (CH aryl) 159.22 (q, aryl), 196.81 (CH, aldehydic). FT-IR (NaCl plates, no nujol): 741w,

25   775w, 834w, 1167 and 1181 weak doublet, 1214 and 1231 w doublet, 1283s, 1378m, 1484s, 1589w, 1654vs (Carbonyl stretch), 2928s and 2960vs (CH stretch). EI-MS: 248, 10%, $[M^+]$. Calculated for $C_{16}H_{24}O_2$: 77.37%C, 9.74%H. Found: 77.54%C, 10.05%H.

30

Synthesis – 5-nonyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholin-4-yl methane (15.95g, 0.11mol) and 5-nonyl-Salicylaldehyde (24.8g, 0.1mol) were placed in a 500ml three-necked round bottomed flask and dissolved in acetonitrile (150ml). This solution was heated under reflux in an N_2 atmosphere for 66 hours, after which time solvent was removed under reduced pressure to yield product as a brown oil. Thin layer chromatography (1% methanol in chloroform) revealed that some unreacted aldehyde remained. The product was purified by flash chromatography. NMR (CDCl$_3$) ^{1}H δ: 0.42 – 1.70 (m, 194), 2.54 (s, 4H, morpholinyl), 3.68 (s) and 3.74 (t, J=4.6) 6H, morpholine and benzylic overlapping, 7.35 and 7.51 (m, J=2.4, 2H, aryl), 10.62 (m, J=2.3, 1H). Calculated for $C_{21}H_{33}NO_3$: 72.57%C, 9.57%H, 4.03%N. Found: 70.98%C, 9.48%H, 3.44%N. FT-IR: 610w,667w, 755vs, 801m, 835vw, 864vs, 909s, 969m, 1001m, 1019m, 1071m, 1118vs (dialkyl ether a.s. stretch), 1285s broad, 1381s, 1455vs broad, 1605s, 1651vs,1682vs, 2958vs broad (CH stretch). EI-MS: 347, 25.7% [M$^+$]. Synthesis – 5-tert-Butyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

Ethoxy-N-morpholinyl methane (15.95g, 0.11mol) and %-tert-Butyl Salicylaldehyde (14.8g 0.1mol) were dissolved in acetonitrile (150ml) and heated under reflux in an N_2 atmosphere for 24 hours. Thin layer chromatography (1% methanol in chloroform) revealed residual aldehyde but almost no morpholinyl methane in the reaction mixture, so extra morpholinyl methane (16.00g 0.11mol) was added and the mixture refluxed for a further 66 hours. TLC indicated that all the aldehyde had reacted, solvent was removed on a rotary evaporator yielding crude product as a pale green oil. Yield 39.427g, 140% suggesting that some acetonitrile remains in the oil. Mixture was dissolved in dichloromethane (150ml), washed with water (3 × 60ml) and concentrated in vacuo. NMR (CDCl$_3$) ^{1}H δ: 1.28 (s,9H, nonyl), 2.55 (m, J=4.6, 2H benzylic), 3.69 (m, J=2.1, 8.5H, morpholinyl), 7.03 (s) 7.37 (d, J=2.6) and 7.59 (d, J=2.6) (2H, aryl), 10.23 (s, 0.5H, aldehyde). ^{13}C δ:31.16 (CH$_3$, ^{t}Bu), 33.96 (q, ^{t}Bu), 52.99 (CH$_2$, morpholinyl), 59.34 (CH$_2$, benzylic), 66.65 (CH$_2$, morpholinyl), 81.53 (q, aryl), 88.34 (q, aryl), 125.63 (CH aryl), 133.41 (CH aryl),

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133.41 and 158.60 (q, aryl), 192.59 (CH, aldehydic).   FT-IR: 736w, 864m, 1118vs (dialkyl ether a.s. stretch), 1616m, 1269m, 1298vw, 1364vw, 1396vw, 1457s, 1481s, 1606m, 1653m, 1681s (carbonyl stretch), 2854s and 2960s (CH stretch). FAB-MS: (Matrix: THIO) 422, 3.6%, [M$^+$ + ^{t}Bu + morph + 2H].

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Synthesis – 5-Methyl-3-(morpholin-4-yl methyl) Salicylaldehyde.

5-Methylyl Salicylaldehyde (27.85g, 0,205 mol) and Ethoxy-N-morpholinyl methane (30.45g, 0.210mol) were refluxed together in acetonitrile (150ml) under an N$_2$ atmosphere for 48 hours. Reaction mixture was cooled to room temperature and concentrated in vacuo leaving a green oil. This was dissolved in HCl (2M, 100ml) and extracted in ether (3×80ml).   The aqueous solution was then basified to pH 9 with 1M KOH, forming a yellow precipitate and a green oil. Yield 36.559g, 0.155mol, 75.8%. Calculated for C$_{13}$H$_{17}$NO$_3$: 66.36%C, 7.28%H, 5.95%N, Found: 65.86%C, 7.80%H, 6.82%N. EI-MS: 306, 1.3% [M$^+$ + 2CO + CH$_3$], FT-IR: 617m, 804m, 863vs, 909s, 953m, 994s, 1031m, 1071m, 1116vs (ether a.s. stretch), 1260vs, 1456 and 1472 vs doublet, 1498s, 1606vs, 1652vs (carbonyl stretch), 1682vs 2339 and 2359 w doublet, 2731w (aldehye CH stretch), 2852vs and 2960vs broad (CH stretch).

Synthesis – N,N′ - bis [5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde] ethelene diamine (ligand 12)

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.824g, 8.13mmol) was dissolved in diethyl ether (30ml) and poured into a solution of ethylene diamine (0.243g, 4.05mmol) in ethanol (30ml). The colour instantly changed to yellow and after stirring overnight the resulting solution was concentrated in vacuo to give crude product as a yellow oil.

Synthesis – N,N′ - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane. (ligand 13) (ligand 13)

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5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (3.30g, 9.50mmol) was dissolved in diethyl ether (30ml) and poured into a solution of diamino propane (0.348g, 4.70mmol) in ethanol (30ml), forming a yellow solution. Removing solvent in vacuo gave crude product as a yellow oil.

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Synthesis – N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] trans – 1,2 – diamino cyclohexane (ligand 14).

5-Nonyl-3-(morpholin-4-yl methyl) salicilaldehyde (2.92g, 8.40mmol) was
10   dissolved in diethyl ether (30ml) and poured into a solution of trans – 1,2 – diamino cyclohexane (0.474g, 4.15mmol) in ethanol (30ml) to form a yellow solution. This was concentrated in vacuo to give the crude product as a yellow oil. $C_{48}H_{76}N_4O_4$

15   Characterisation of – N,N' - bis [5-Nonyl -3-(morpholin-4-yl methyl) salicilaldehyde] ortho – Phenylene diamine (ligand 15).

The initial crude product was isolated as a viscous oil. Any remaining water-soluble impurities were extracted with water. The chloroform solution was
20   evaporated to dryness and the product dried in-vacuo to yield a highly viscous yellow oil. (Found: C, 67.19; H, 8.25; N, 6.90. Calc. for $C_{48}H_{70}N_4O_4.(CHCl_3)$: C, 66.39; H, 8.07; N, 6.32%). δ_H (CDCl$_3$, 200 MHz): 0.5-1.69 (m, 19H, C_9H_{19} mixed isomer chain), 2.53 (s, 4H, NCH$_2$CH$_2$O), 3.72 (m, 6H, OCH$_2$CH$_2$N + Ar-CH$_2$N), 6.77 (m, 1H, Ar-H), 7.07 (m, 1H, Ar-H), 7.24-7.37 (m, 2H, Ar-H), 8.65 (s, 1H,
25   CH=N), 13.50 (br, 1H, OH). δ_C (CDCl$_3$): 10-63 (C_9 mixed isomer chain), 52.8 (NCH$_2$CH$_2$O), 66.60 (NCH$_2$CH$_2$O), 66.70 (CCH$_2$N), 110.4 (Ar C), 114.6 (Ar C), 115.5 (Ar C), 118.1 (Ar C), 118.5 (Ar CH), 119.0 (Ar CH), 119.6 (Ar CH), 122.2 (Ar CH), 123.5 (Ar C), 127.2 (Ar CH), 127.7 (Ar CH), 153.6 (Ar C), 157.3 (CHN). MS (FAB, thioglycerol) m/z 768 (MH$^+$, 90%).

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Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] ortho – Phenylene diamine (ligand 11).

Ortho – phenylene diamine (2.163g, 20mmol) was dissolved in ethanol (150ml). The flask was wrapped in tin fiol to protect the material from light. This was added to a solution of 5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde (10.86g, 39.2mmol) in ether (150ml), again in the dark. After stirring for ca. 10

5   minutes the solution was concentrated in vacuo to leave a dark brown oil, crude yield = 11.36g, 18.4mmol, 93%. This was dissolved in hexane/ether 2:1 (ca 300ml). A small amount of brown solid remained undissolved and was removed by filtration. The solvent was allowed to evaporate slowly from a 500ml conical flask to leave a semi-crystalline orange material. This was dried

10   under vacuum (oil pump) for 18 hours. Yield = 10.07g, 16.1mmol, 83.8%. FAB-MS 627, 8.5%, [MH$^+$], FT-IR (NaCl plates): 743m, 803w, 863m, 880w, 909w, 1005w, 1017vw, 1038w, 1070w, 1117vs (dialkyl ether a.s stretch), 1192vw, 1205vw, 1270vw, 1300w, 1362w, 1394w, 1456m, 1482m, 1494m, 1590m, 1616m (conjugated imine), 2856s and 2959vs (CH stretch), 3361s, broad,

15   NMR (CDCl$_3$), ^{1}H δ: 1.18-1.34 (m, J=8 and J=12, 9H, ^{t}Bu), 2.46 – 2.57 (m, J=4.6, 4H, morpholine), 3.62-3.76 (m, J=7.0, morph + benzylic 6H), 6.68 – 7.43 (3m's, J= 1.4, 1.2, 2.0, 4H, aryl), 8.67 (s, ½H, imine).

Synthesis of N,N'-bis [5-tert-Butyl-3-(piperidyl methyl) salicilaldeyde]-2,2'-

20   diphenylene diamine (ligand 19).

To a stirred solution of 2-hydroxy-3-(piperidinyl-4-ylmethyl)-5-tert-butylbenzaldehyde (1.908 g, 6.93 mM) in ether (20 cm^3) was added a solution of 2,2'-diaminobiphenyl (0.638 g, 3.46 mM) in acetone (20 cm^3). The yellow

25   solution was stirred overnight and concentrated in-vacuo to yield a pale yellow powder, which was recrystallised from acetone (1.407 g, 58%). Found: C, 78.96; H, 8.40; N, 7.90. Calc. for C$_{46}$H$_{58}$N$_4$O$_2$: C, 79.04; H, 8.36; N, 8.02%. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 1.24 (s, 9H, C(CH$_3$)$_3$), 1.42 (d, ^{3}J$_{HH}$ 4.4 Hz, 2H, NCH$_2$CH$_2$CH$_2$), 1.58 (t, ^{3}J$_{HH}$ 4.4 Hz, 4H, NCH$_2$CH$_2$CH$_2$), 2.41 (s, 4H,

30   NCH$_2$CH$_2$CH$_2$), 3.51 (s, 2H, Ar-CH$_2$N), 7.10-7.44 (m, 6H, Ar-H), 8.50 (s, 1H, N=CH). ^{13}C NMR (CDCl$_3$, 200 MHz): δ 24.19 (NCH$_2$CH$_2$CH$_2$), 25.88 (NCH$_2$CH$_2$CH$_2$), 31.28 (CH$_3$), 33.76 (C(CH$_3$)$_3$), 54.03 (NCH$_2$CH$_2$CH$_2$), 56.93 (CCH$_2$N), 118.08 (Ar C), 118.6 (Ar C), 124.3 (Ar C), 126.10 (Ar CH), 126.44 (Ar

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CH), 128.63 (Ar CH), 130.72 (Ar CH), 131.04 (Ar CH), 134.5 (Ar C), 140.46 (Ar C), 147.9 (Ar C), 153.8 (Ar C), 162.08 (CHN). MS (FAB, NOBA) 699 m/z, (MH$^+$ 75%).

5   Characterisation of N,N' - bis [5 - nonyl - 3 - (piperidyl methyl) salicilaldehyde] 2,2'-diphenylene diamine (ligand 21)

This bright orange solid was isolated from the crude product after water-soluble impurities were removed by extraction with water (3.45 g, 95%). (Found: C, 10   80.16; H, 9.18; N, 6.71. Calc. for $C_{56}H_{78}N_4O_2$: C, 80.14; H, 9.37; N, 6.68 %). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.48-1.37 (m, 19H, C_9H_{19} mixed isomer chain), 1.42 (s, 2H, NCH$_2$CH$_2$CH$_2$), 1.56 (s, 4H, NCH$_2$CH$_2$CH$_2$), 2.39 (s, 4H, NCH$_2$CH$_2$CH$_2$), 3.52 (s, 2H, Ar-CH$_2$N), 7.07-7.43 (m, 6H, Ar-H), 8.53 (s, 1H, CH=N), 12.5 (br, 1H, OH). ^{13}C NMR (CDCl$_3$, 200 MHz): δ 24.81 (NCH$_2$CH$_2$CH$_2$), 26.53 15   (NCH$_2$CH$_2$CH$_2$), 31.28 (CH$_3$), 33.76 (C(CH$_3$)$_3$), 54.58 (NCH$_2$CH$_2$CH$_2$), 57.36 (CCH$_2$N), 116.2 (Ar CH), 118.8 (Ar CH), 119.1 (Ar CH), 125.0 (Ar C), 126.6 (Ar CH), 129.08 (Ar CH), 131.4 (Ar CH), 135.1 (Ar C), 137.8 (Ar C), 139.8 (Ar C), 148.2 (Ar C), 157.5 (Ar C), 162.8 (CHN). MS (FAB, thioglycerol) m/z, (MH$^+$ %).

20   <u>Complexation</u>

Complexation studies using ligands of the invention and various metal salts were carried out using the following general method. A solution of ligand (0.3 mM) in methanol (20 cm^3) was stirred together with a solution of the 25   appropriate metal salt MX$_n$ (1 M equiv.) in methanol (20 cm^3) overnight. Colour changes due to complex formation were generally instantaneous. After removal of the solvent in-vacuo the products were recrystallised as indicated and air-dried.

30   [Ni(8)SO$_4$], MX$_n$ = NiSO$_4$.6H$_2$O. Recrystallisation from MeOH:H$_2$O, 3:1 gave a red microcrystalline material formulated as [Ni(1)SO$_4$]·6H$_2$O (0.59 g, 93.6 %). m.p. 235-240 °C. (Found: C, 48.86; H, 7.37; N, 6.53. Calc. for $C_{34}H_{62}N_4NiO_{14}S$: C, 48.53; H, 7.43; N, 6.66%).χ$_m$ = 1.14 × 10^{-9}, μ$_{eff}$ = 0. δ$_H$ (CDCl$_3$, 200 MHz):

1.27 (m, 9H, C(CH$_3$)$_3$), 2.6-3.3 (br, 4H, NCH$_2$CH$_2$O), 3.49 (s, 2H, NCH$_2$CH$_2$N), 3.7-4.2 (br, 4H, NCH$_2$CH$_2$O), 4.3 (s, 2H, Ar-CH$_2$N), 7.21 (d, 1H, ^{4}J$_{HH}$ 2.5 Hz, Ar-H), 7.29 (d, 1H, ^{4}J$_{HH}$ 2.5 Hz, Ar-H), 7.67 (s, 1H, N=CH). MS (FAB, thioglycerol) m/z 733 (MH$^+$, 10%). ν_{max}/cm^{-1} 1119vs (SO$_4$).

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[Ni(8-2H)], MX$_n$ = Ni(CH$_3$CO$_2$)$_2$.4H$_2$O. Recrystallisation from diethylether gave an orange/red microcrystalline material formulated as [Ni(1-2H)]·2H$_2$0 (0.167 g, 73%) m.p. 235-240 °C. Found: C, 61.00; H, 7.38; N, 8.19. Calc. for C$_{34}$H$_{52}$N$_4$NiO$_4$: C, 60.77; H, 7.75; N, 8.34%. χ_m = 2.47 × 10^{-10}, μ_{eff} = 0. δ_H (CDCl$_3$,

10   200 MHz): 1.24 (m, 9H, C(CH$_3$)$_3$), 2.53 (t, 4H, ^{4}J$_{HH}$ 4.4 Hz, NCH$_2$CH$_2$O), 3.35 (s, 2H, NCH$_2$CH$_2$N), 3.61 (s, 2H, Ar-CH$_2$N), 3.73 (t, 4H, ^{3}J$_{HH}$ 4.4 Hz, NCH$_2$CH$_2$O), , 6.89 (d, 1H, ^{4}J$_{HH}$ 2.6 Hz, Ar-H), 7.37 (d, 1H, ^{4}J$_{HH}$ 2.6 Hz, Ar-H), 7.46 (s, 1H, N=CH). MS (FAB, thioglycerol) m/z 636 (MH$^+$, 50%).

15   [Ni(8)(NO$_3$)$_2$], MX$_n$ = Ni(NO$_3$)$_2$.6H$_2$O. Recrystallisation from diethylether gave an orange/red microcrystalline powder formulated as [Ni(1)(NO$_3$)$_2$]·3H$_2$O (0.253 g, 91%) m.p. 200-204 °C. Found: C, 49.79; H, 6.35; N, 10.76. Calc. for C$_{34}$H$_{56}$N$_4$NiO$_{13}$: C, 50.11; H, 6.88; N, 10.31%. χ_m = 2.11 × 10^{-10}, μ_{eff} = 0. δ_H (CDCl$_3$, 200 MHz): 1.24 (m, 9H, C(CH$_3$)$_3$), 3.21 (br, 4H, NCH$_2$CH$_2$O), 3.45 (s,

20   2H, NCH$_2$CH$_2$N), 3.91 (br, 4H, NCH$_2$CH$_2$O), 4.23 (s, 2H, Ar-CH$_2$N), 7.22 (d, 1H, ^{4}J$_{HH}$ 2.1 Hz, Ar-H), 7.49 (d, 1H, ^{4}J$_{HH}$ 2.1 Hz, Ar-H), 7.65 (s, 1H, N=CH). ν_{max}/cm^{-1} 1366vs and 1398vs (NO$_3$). MS (FAB, thioglycerol) m/z 699 (MH$^+$, 4%).

[Cu(8)SO$_4$], MX$_n$ = CuSO$_4$.5H$_2$O. Recrystallisation from EtOH:ether, gave a
25   dark brown crystalline material formulated as [Cu(1)SO$_4$]·5H$_2$O (0.111 g, 43%). m.p. 268-270 °C. (Found: C, 51.96; H, 7.05; N, 6.33. Calc. for C$_{34}$H$_{60}$N$_4$CuO$_{13}$S: C, 52.44; H, 7.77; N, 6.80%). ν_{max}/cm^{-1} 1119vs (SO$_4$). MS (FAB, NOBA) m/z 734 (MH$^+$, 30%).

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Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (ligand 9) Nickel Sulphate complex.

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Nickel Sulfate heptahydrate (104mg, 0.37mmol) was dissolved in hot methanol (20ml) and added to a hot solution of N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (200mg,0.37mmol) in methanol (30ml). Mixture instantly turned brown. 20ml of solution was removed and
5   concentrated in vacuo leaving a glassy brown solid, the remainder was left to stand in a sealed conical flask. The solid was crystallised in ether and recovered by filtration, yield = 95mg. Assuming sample is representative of whole solution, yield = 238mg, 0.32mmol, 86%.

10 Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] diamino propane (ligand 9) Nickel Nitrate complex.

Nickel Nitrate hexahydrate (85mg, 0.37mmol) in methanol (20ml) was added to a hot solution of N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl)
15 salicilaldehyde] diamino propane (200mg,0.37mmol) in methanol (30ml), changing colour to brown. After stirring for ca. 5 minutes, 15ml solution was removed and concentrated invacuo and the rest was put aside to stand in a sealed conical flask. Removing the solution gave a brown amorphous solid which was crystalised in ether and recovered by filtration.
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Synthesis – N,N' - bis [5-tert-Butyl-3-(morpholin-4-yl methyl) salicilaldehyde] Ortho- Phenylene diamine Nickel Sulfate complex.

A small amount of ligand (037g, 0.6mmol) was dissolved in methanol and
25 stirred up with stoichiometric amount of nickel sulfate (1669mg, 0.6mol) forming a red brown solution. The solvent was removed in vacuo leaving a brittle red brown glass This was ground to a powder and found to be soluble in polar and chlorinated solvents, sparingly soluble in toluene and insoluble in hexane.
30

Solvent extraction and stripping

Solvent extraction and stripping of anions and cations is illustrated with

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reference to the following example involving copper sulfate complexed with ligand 21.

A 0.01 M chloroform solution of ligand 21 (20 cm^3) was intimately mixed with a 1 M aqueous solution of CuSO$_4$ (20 cm^3) for 24 h at room temperature. The chloroform solution turned dark brown almost immediately. A sample was removed for ICP-EAS analysis to determine the copper and sulfur content. The remaining organic solution was washed with an aqueous solution (17 cm^3) adjusted to pH 1.5 with H$_2$SO$_4$ for 24 h. At this time the dark brown colour had bleached and the copper and sulfur content was again examined by ICP-EAS. The remaining organic solution was washed with an aqueous solution adjusted to pH 10 with ammonia for 24 h at which point the copper and sulfur content was examined by ICP-EAS. The chloroform solution was isolated and contacted with a 1 M aqueous solution of CuSO$_4$ (15 cm^3) for 24 h. The final copper and sulfur content of the organic phase was then determined. The percentage of copper and sulfate in the chloroform phase after each stage are displayed in the table below:

	Loading	Acid wash	Ammonia wash	Reloading
%Cu	83	22	23	73
%SO$_4$	136	85	0	115

These results confirm that the ligand can be taken through a cycle of loading and stripping as represented in the scheme below. They also confirm the ability to fine-tune these ligands to suit a particular metal salt combination. In these experiments a biphenyl-bridged ligand 21 was used to encourage a tetrahedral metal binding environment so that copper binding is weakened favouring removal by acid stripping.

23
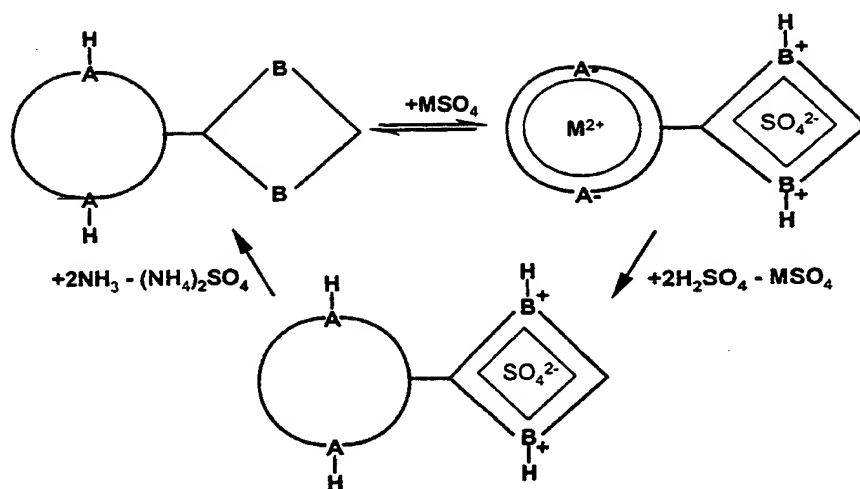
CLAIMS

1.   A method of extracting both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the steps of: contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s); selectively stripping and recovering said cation(s) and said anion(s) from said complex; and recovering said ligand, free of said cation(s) and anion(s), for future use.

2.   A method according to claim 1, wherein the ligand has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, the method involving the steps of: adding a said water-immiscible extraction medium to said aqueous medium, whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in a water-immiscible phase; and separating said water-immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.

3.   A method according to claim 1, wherein the ligand is immobilised on or within a solid support.

4.   A method according to any of claims 1 to 3, wherein the ligand is of the following formula:
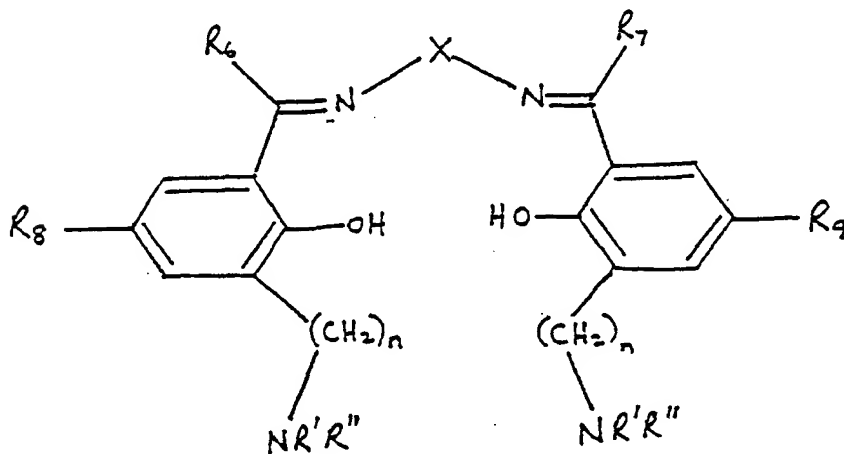
24
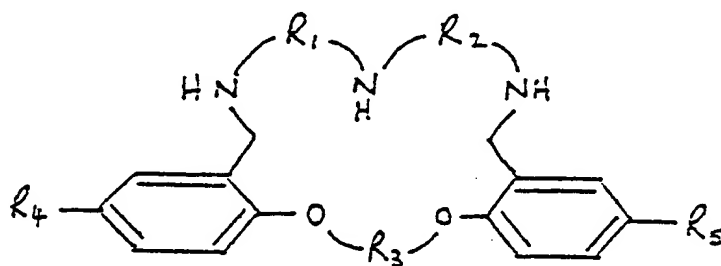
where R_1, R_2 and R_3 are, independently, substituted C_2 to C_4 linkages; and

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

5.   A method according to claim 4, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

6.   A method according to any of claims 1 to 3, wherein the ligand has a cation binding site comprising at least one coordinating acid group and an anion binding site comprising at least one protonatable base.

7.   A method according to claim 6, wherein the ligand has the following formula:

where: X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

R_6, R_7, R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

R'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

8.   A method according to claim 6 or claim 7, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electrolysing the resulting solution to product elemental metal.

9.   A method according to claim 8, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

10.   A method according to any of claims 7 to 9, wherein NR'R" is a morpholine or piperidine ring.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C02F1/68   C02F1/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 36 07 982 A (LOTTERMOSER MANFRED) 17 September 1987 (1987-09-17) claim 1	1,2

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 July 2000	11/07/2000

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Fouquier, J-P

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3607982 A	17-09-1987	NONE	